



Ion-molecule reactions of CI2 with CI- and F-

Lucia M. Babcock and Gerald E. Streit

Citation: The Journal of Chemical Physics **76**, 2407 (1982); doi: 10.1063/1.443269 View online: http://dx.doi.org/10.1063/1.443269 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/76/5?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Ion–Molecule Reactions in Olefins J. Chem. Phys. **52**, 282 (1970); 10.1063/1.1672680

Ion—Molecule Reactions in Propane J. Chem. Phys. **46**, 4084 (1967); 10.1063/1.1840490

Exothermic Ion—Molecule Reactions J. Chem. Phys. **45**, 3837 (1966); 10.1063/1.1727408

Ion—Molecule Reactions of Methane J. Chem. Phys. **45**, 1925 (1966); 10.1063/1.1727873

Negative IonMolecule Reactions J. Chem. Phys. **31**, 1426 (1959); 10.1063/1.1730618



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.89.98.137 On: Sat, 29 Nov 2014 18:50:24

Ion-molecule reactions of Cl₂ with Cl⁻ and F^{- a)}

Lucia M. Babcock and Gerald E. Streit

University of California, Los Alamos National Laboratory, Los Alamos, New Mexico 87545 (Received 17 August 1981; accepted 12 November 1981)

Using the flowing afterglow technique, we have examined the process $Cl_2 + Cl^- \rightarrow Cl_3^-$ in helium buffer gas. The system was studied over a range of helium pressures and the dependence of the apparent two-body rate upon the buffer gas concentration gives a three-body rate constant for the process: $k = 0.9 \times 10^{-29}$ cm⁶ molecule⁻² s⁻¹. In addition, we looked at the analogous process involving a fluoride ion. There is no evidence for formation of the trihalide Cl_2F^- under our experimental conditions. A charge exchange process between Cl_2 and F^- to produce Cl^- and neutral CIF does occur, however. This rate is independent of the pressure of the helium buffer gas: $k = 8.8 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

I. INTRODUCTION

The interhalogens are a fascinating group of chemical compounds, with as many as seven other halogens bonded to a single central halogen atom. Because the normal halogen atom contains seven valence shell electrons, none of the interhalogens, with the exception of the diatomic species, conform to the Lewis octet description of covalent bonding. As such, these polyvalent halogen compounds have received a great deal of theoretical, $^{1-4}$ and experimental attention.⁵⁻⁸ The triatomic X_3 and X_3 are the first compounds in the interhalogen series to contain more than the Lewis octet number of valence electrons, 21 and 22, respectively. The neutral trihalogen radicals I₂F and ClIF have been produced in crossed molecular beams,⁹ and Ungemach and Schaefer³ have predicted that the ClF_2 radical has a C_{2v} structure. The trihalide anions X_3^- are closed shell species having 22 valence electrons. X-ray studies of some trihalide salts have shown them to be linear and of D_{mh} symmetry.¹⁰ In addition, *ab initio* calculations by Guest et al.² predict a linear geometry for the trihalide anion ClF_2 .

Bonding with the trihalide ions have been postulated as containing a large amount of ionic character. This has been supported both by experimental work^{5,6} and by calculations.^{1,2} One way of viewing this is that there is considerable contribution to the overall bonding from resonance structures of the type $X - X \cdots X^- + X^- \cdots X - X$. In molecular orbital terms, this is a three-center, fourelectron bond. The significant degree of ionic character and the idea of the three-center, four-electron bond have been invoked in descriptions of other compounds containing so-called "expanded octets," notably SF_6 , ¹¹ SF_4 , ¹² and the rare gas dihalide ArCIF.¹³ With this picture of bonding in the trihalides, one need not invoke excited *d* orbitals on the central halogen atom (that is, invoke a dsp^3 hybrid). Rather, the additional electrons are accommodated by the halogen *p* orbitals.

The trihalide anions are also of interest since they are isoelectronic with the various rare gas dihalides. For example, Cl_3^- is the isoelectronic analog of $ArCl_2$. Rare gas compounds of this type have generated much interest, and it is possible that some insight may be gained through a study of the analogous ion-molecule processes.

Although x-ray studies¹⁰ identified the trihalide species some time ago and Cl_3^- was characterized in solution^{14,15} over 20 years ago, there is a paucity of experimental data on gas phase reactions of the trihalide ions. Melton *et al.*¹⁶ mention the observation of Br₃⁻ and Cl₃⁻ in mass spectroscopic studies, and Hughes *et al.*¹⁷ postulate Cl₃⁻ as an intermediate in the charge exchange reaction between Cl⁻ and Cl₂. Formation of Cl₃⁻ and Br₂Cl⁻ in rare gas-halogen mixtures have been reported, ¹⁸ but rate studies were not performed. Rate coefficients for the three-body addition of Br⁻ to Br₂ have been measured using Ar¹⁹ and Br₂²⁰ as the bath gas.

We have examined the reactions of Cl_2 with both $Cl^$ and F^- . The reaction with chloride ion is a three-body addition in which the product is the trihalide ion Cl_3^- . The analogous reaction $Cl_2 + F^-$ does not produce the trihalide, but instead undergoes a charge exchange reaction to produce Cl^- ion and presumably neutral ClF. Photodestruction cross section work by Lee *et al*.²¹ has shown Cl_3 to have a high electron affinity; their estimate is 5.14 eV. This agrees with the limit E.A. $(Cl_3) \ge 3.8 \text{ eV}$ determined by Robbiani and Franklin, ²² who also calculate a value for the heat of formation for Cl_3^- of -3.11eV.

II. EXPERIMENTAL

All experiments were carried out at ambient temperatures using the flowing afterglow apparatus previously described.^{23,24} The gases used as sources for both reactant neutrals and reactant ions were obtained commercially and used without further purification. In all cases, the buffer gas employed was helium, which was passed through a molecular sieve maintained at 77 K to trap any condensable impurities. Typically, the helium flow was maintained at 180 atm cm³ s⁻¹.

The reactions studied were those between neutral Cl_2 and the Cl⁻ and F⁻ ions. Reactant negative ions were produced via dissociative electron attachment to an appropriate neutral gas. Chloride ions were generated from dissociative attachment to Cl_2 , CCl_4 , or CF_3Cl . Fluoride ions were produced by dissociative attachment to F_2 or CF_3Cl . When CCl_4 and CF_3Cl were used as sources of Cl^- , the results, as expected, were indepen-

^{a)}Work performed under the auspices of the U.S. Department of Energy.

dent of the neutral source gas. In the case of production of Cl⁻ from Cl₂, the presence of large amounts of Cl₂ (both as the ion source gas and also as neutral reactant) had adverse effects upon the detection system. This made it preferable to use either CCl₄ or CF₃Cl as precursors for reactant chloride ion. To carry out kinetic studies of the $Cl_2 + F^-$ charge exchange reaction it was found necessary to generate F⁻ from CF₃Cl, rather than from F_2 . The neutral product of this charge exchange is presumable ClF. When F_2 is used as a source of F^{*}, it appears that an equilibrium situation may be established. A reasonable explanation is that a concurrent neutral reaction involving F atoms generated in the dissociative attachment process and Cl₂ produces enough ClF to set up equilibrium conditions. Alternatively, the curvature in the experimental data could be due to production of F⁻ via a chain reaction:

$$\mathbf{F}^{-} + \mathbf{Cl}_2 \rightarrow \mathbf{ClF} + \mathbf{Cl}^{-} , \qquad (1)$$

$$Cl^{-} + F_{2} \rightarrow ClF + F^{-} .$$
 (2)

Production of F^{-} from a neutral other than F_{2} makes it impossible for either of these reactions to occur. Indeed, when $CF_{3}Cl$ is used to make F^{-} , the curvature disappears from the kinetic data.

Rate information is obtained by monitoring the reactant ion signal as a function of added neutral reactant. Apparent two-body rate coefficients are obtained, as discussed previously, ^{24,25} under conditions of fixed flow velocity and reaction distance. In order to obtain a three-body rate coefficient for the reaction $Cl_2 + Cl^-$ in helium, the apparent two-body rates were measured over the pressure range 0.2–2.0 Torr. Measured twobody rate coefficients are reported with a precision of $\pm 10\%$; the accuracy is believed to be $\pm 30\%$.

III. RESULTS AND DISCUSSION

A. $Cl_2 + Cl^-$ termolecular addition

When neutral Cl_2 reacts with Cl^- ions in the flowing afterglow, the main product ion is Cl_3^- . We examined this addition reaction in helium buffer gas over a wide range of pressures. The apparent two-body rate constants measured at various pressures of helium are presented in Table I. It is clear that the measured twobody rate coefficient is a function of the helium concen-

TABLE I. Apparent two-body rate constants for $Cl_2 + Cl^-$ in helium.^a

P (Torr)	k _{app} (cm ³ molecule ⁻¹ s ⁻¹)	$\frac{k_{app}}{(\text{He})}$ (cm ⁶ molecule ⁻² s ⁻¹)
0.91	2.9×10 ⁻¹³	1.0×10^{-29}
1.12	3.5×10^{-13}	0.9×10^{-29}
1.31	3.9×10^{-13}	0.9×10^{-29}
1.51	4.7 \times 10 ⁻¹³	0.9×10^{-29}
1.71	5.2×10 ⁻¹³	0.9×10^{-29}

^aThe values for k_{app} at a given pressure P are averages of more than one run, in most instances.



FIG. 1. The apparent two-body rate constant for the reaction $Cl_2 + Cl^-$ in helium is plotted as a function of helium pressure.

tration. This is typical of a three-body reaction in which the addition complex is collisionally stabilized by some third body. This termolecular process can be représented by the following scheme:

$$Cl_2 + Cl^{-} \frac{k_1}{k_{-1}} (Cl_3^{-})^*$$
, (3)

$$(Cl_3^-)^* + He \xrightarrow{k_2} Cl_3^- + He \quad . \tag{4}$$

If one assumes steady state conditions for $(Cl_3^-)^*$, the rate coefficient for the above sequence is

$$k_{app} = \frac{k_1 k_2 (\text{He})}{k_{-1} + k_2 (\text{He})} .$$
 (5)

For low pressures (that is, low concentrations of He) such as those employed in flowing afterglow studies, the assumption $k_2(\text{He}) \ll k_{-1}$ is valid, and Eq. (3) reduces to

$$k_{app} = \frac{k_1 k_2 (\text{He})}{k_{-1}}$$
 (6)

This form of the rate coefficient predicts a linear dependence of the apparent two-body rate upon the He concentration, with a zero intercept. Figure 1 presents our values of k_{app} plotted as a function of the helium pressure. As expected, the plot is linear with zero intercept. There is no evidence for a pressure independent mechanism by which Cl⁻ reacts (this would be apparent if the intercept of Fig. 1 were nonzero). The slope of the line in Fig. 1 is given by $(k_1 k_2)/k_{-1}$; thus the three-body rate extracted from the slope contains the equilibrium constant k_1/k_{-1} , as well as the collisional stabilization rate coefficient. The termolecular rate coefficient, $k^{(3)} = (k_1 k_2)/k_{-1}$, which we extract from our data for the addition of Cl⁻ to Cl₂ with helium as the third body, is $k^{(3)} = 0.9 \times 10^{-29}$ cm⁶ molecule⁻² s⁻¹.

Hughes *et al*.¹⁷ have measured the rate coefficient for the two-body formation of Cl_3 from Cl_2 and Cl_2 :

$$\mathrm{Cl}_2^- + \mathrm{Cl}_2 \to \mathrm{Cl}_3^- + \mathrm{Cl} \quad . \tag{7}$$

Their value is $k = 8.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In addition, photodissociation studies^{21,26} have been carried out on the Cl₂ ion. However, in the flowing afterglow experiments Cl₂ was never detected, therefore, it is

J. Chem. Phys., Vol. 76, No. 5, 1 March 1982

unlikely that Reaction (7) contributed significantly to Cl_3 formation in our studies.

At the highest pressure accessible, about 2 Torr, we saw no evidence for clusters of Cl_3^- with Cl_2 , even though the Cl_3^- signal declined, indicating that it was reacting further. It is interesting to note that a cluster ion which was detected had a mass consistent with $Cl_3^- \cdot CO_2$, although CO_2 would be present only as a trace contaminant. Switching reactions, of which there are many examples,²⁷ are those in which one neutral preferentially replaces another in an ion cluster:

$$A^{-} \cdot B + C \rightarrow A^{-} \cdot C + B \quad . \tag{8}$$

Because Cl_3^- declines as Cl_2 is added, it is possible that $Cl_3^- \cdot Cl_2$ is initially formed, and that a subsequent switching reaction in which CO_2 replaces Cl_2 takes place. This certainly warrants further investigation.

B. Cl₂ + F⁻ bimolecular reaction

We examined the reaction of Cl_2 with fluoride ions over the same range of pressures used in the $Cl_2 + Cl^$ studies. There was no evidence of the termolecular addition reaction to produce Cl_2F^- ; the product ion Cl_2F^- was not observed, and the rate of decay of the reactant F^- ion was independent of the pressure of helium.

The reaction which occurs is the charge exchange reaction is

$$Cl_2 + F^- \rightarrow Cl^- + ClF \quad . \tag{9}$$

When F_2 was used as the source gas for F⁻, the ion signals, as a function of added Cl_2 , looked like the data presented in Fig. 2. The curvature of the F⁻ signal at high flows of Cl_2 was more pronounced for the runs which were done at higher pressures. This type of behavior can be indicative of an equilibrium system; in this case,

$$Cl_2 + F^{-} \neq Cl^{-} + ClF \quad . \tag{10}$$

For equilibrium conditions to obtain, it is required that the energetics of the forward and reverse reactions be close to zero, and that there be enough neutral product present to set up the equilibrium conditions. In the case presented above, the first requirement is met. Using $D(C1-C1) = 2.52 \text{ eV}, {}^{28}D(C1-F) = 2.64 \text{ eV}, {}^{28}E.A.(C1)$ = 3.61 eV, 29 and E.A.(F) = 3.40 eV, 30 one calculates that the overall $\triangle H$ for reaction is only -0.33 eV. In general, the amount of neutral product formed in flowing afterglow experiments is so much less than the amount of neutral reactant, that even a system whose energetics support an equilibrium situation will not reach equilibrium conditions unless there is an additional source of the product neutral. When F_2 is used to produce F⁻ via dissociative electron attachment, F atoms are also produced. It is possible that these react with neutral Cl_2 to produce enough ClF to establish the equilibrium system shown in Reaction (10). The curvature could also result from a downstream source of F^{-} ions. The chain reaction presented in Eqs. (1) and (2) would be such a source. Both steps are exothermic and would be predicted to proceed under the



thermal conditions of our experiments. As the concentration of Cl_2 is increased, the F⁻ signal would increase also. Either of these explanations could account for the curvature seen when F_2 is the neutral precursor for F⁻.

Fluoride ion can also be produced by dissociative attachment of electrons to CF_3Cl . There is no path by which the neutral can effectively produce CIF. In addition, removing F_2 from the system prevents the chain reaction from proceeding. Figure 3 shows the ion signals for the reaction of $F^{\text{-}}$ with Cl_2 where CF_3Cl is the ion source gas. The experimental conditions are the same as those used in obtaining the data in Fig. 2. Clearly, the curvature in the F⁻ ion signal at high Cl₂ flows is not present. Using CF₃Cl to make F⁻, we were able to obtain a rate constant for the charge exchange reaction between Cl₂ and F⁻: $k = 8.8 \times 10^{-10}$ cm³ mole $cule^{-1}s^{-1}$. This rate coefficient was found to be independent of the pressure of the helium buffer gas. The absence of pressure dependence supports the conclusion that the three-body reaction to produce Cl₂F⁻ does not occur to any appreciable degree.

IV. SUMMARY AND CONCLUSIONS

In our studies, the only reaction which we have found to occur between Cl_2 and F is a charge exchange reac-





FIG. 3. As in Fig. 2, ion signals for the reaction $Cl_2 + F^-$ as a function of Cl_2 flow are given. In this case, however, F^- is made from CF_3Cl , and there is no evidence for an equilibrium situation. Experimental conditions were as follows: $F_{He} = 180 \text{ atm cm}^3 \text{s}^{-1}$, P = 0.50 Torr.

tion which produces Cl⁻ and ClF. Our value of the rate coefficient for this reaction is $k = 8.8 \times 10^{-10}$ cm³ mole-cule⁻¹ s⁻¹.

For the termolecular addition of Cl^- to Cl_2 in helium we find a value for the rate constant of $k = 0.9 \times 10^{-29}$ $cm^6 molecule^{-2} s^{-1}$. Even at the highest accessible pressures (about 2 Torr) we see no evidence of higher clusters of the general formula $Cl_3 \cdot (Cl_2)_n$. Fehsenfeld and Ferguson^{27(b)} have looked at the clustering of Cl to H₂O and to SO₂. They find that the rate of clustering to H_2O is considerably slower (2×10⁻²⁹ cm⁶ molecule⁻² \times s⁻¹) than to SO₂ (1×10⁻²⁸ cm⁶ molecule⁻² s⁻¹), and they attribute this to a stronger bonding in the case of SO₂. The chemically bonded species Cl₃ is known both from early solution studies^{14,15} and from matrix isolation work.³¹ The order of magnitude of our rate coefficient and the known existence of a chemically bonded Cl. ion are strong evidence that the product of our addition reaction is not simply an associated $Cl_2 \cdot Cl^-$ complex. As mentioned in the introduction, the trihalide ions are isoelectronic with the rare gas dihalides. In particular, Cl_3 is isoelectronic with $ArCl_2$. It is interesting to note then, that in a laser photolysis study of matrix isolated halogens, Howard and Andrews³² see no evidence for any complex formation in $Ar: Cl_2$ matrices. There has, however, been a study of ArClF¹³ (the trihalide analog

of which would be Cl_2F^-), and it is found that in ArClF there is strong evidence for "incipient covalent bonding." However, the bond order and bond lengths are still more characteristic of a van der Waals molecule than of a chemical bond. In view of this, it would be interesting to delve more deeply into the trihalide ion chemistry, and to see what may be gained by a comparison of these ions with their isoelectronic rare gas-dihalide analogs. While there may be general similarities, it may be impossible to make extended comparisons between the two sets of chemical species. With this caution in mind, it is interesting to note that, while the Cl_3^- ion is known, its neutral analog $ArCl_2$ is not known, and that although ArClF has been prepared and studied, its anionic analog Cl_2F^- does not exist.

- ¹G. C. Pimentel, J. Chem. Phys. 19, 446 (1951).
- ²M. F. Guest, M. D. Hall, and I. H. Hillier, J. Chem. Soc. Faraday Trans. 2 69, 1829 (1973).
- ³S. R. Ungemach and H. F. Schaefer III, J. Am. Chem. Soc. 98, 1658 (1976).
- ⁴P. W. Tasker, Mol. Phys. 33, 511 (1977).
- ⁵C. D. Cornwell and R. S. Yamasaki, J. Chem. Phys. 27, 1060 (1957).
- ⁶R. S. Yamasaki and C. D. Cornwell, J. Chem. Phys. 30, 1265 (1959).
- $^7\mathrm{K.}$ O. Christie and J. P. Guertin, Inorg. Chem. 4, 905 (1965).
- ⁸K. O. Christie, W. Sawodny, and J. P. Guertin, Inorg. Chem. 6, 1159 (1967).
- ⁹J. J. Valentini, M. J. Coggiola, and Y. T. Lee, Faraday Discuss. Chem. Soc. 62, 232 (1977).
- ¹⁰R. C. L. Mooney, Z. Krist. A 100, 519 (1939); Phys. Rev. 47, 807 (1935).
- ¹¹T. Kiang and R. N. Zare, J. Am. Chem. Soc. 102, 4024 (1980).
- ¹²L. M. Babcock and G. E. Streit, J. Chem. Phys. 75, 3864 (1981).
- ¹³S. J. Harris, S. E. Novick, W. Klemperer, and W. E.
- Falconer, J. Chem. Phys. 61, 193 (1974). ¹⁴L. I. Katzin, J. Chem. Phys. 20, 1165 (1952).
- ¹⁵G. Zimmerman and F. C. Strong, J. Am. Chem. Soc. 79, 2063 (1957).
- ¹⁶C. E. Melton, G. A. Ropp, and P. S. Rudolph, J. Chem. Phys. 29, 968 (1958).
- ¹⁷B. M. Hughes, C. Lifshitz, and T. O. Tiernan, J. Chem. Phys. **59**, 3162 (1973).
- ¹⁸B. A. Huber and T. M. Miller, J. Appl. Phys. 48, 1708 (1977).
- ¹⁹G. D. Sides, T. O. Tiernan, and R. J. Hanrahan, J. Chem. Phys. 65, 1966 (1976).
- ²⁰F. K. Truby, Phys. Rev. A 4, 114 (1971).
- ²¹L. C. Lee, G. P. Smith, J. T. Mosely, P. C. Cosby, and J. A. Guest, J. Chem. Phys. 70, 3237 (1979).
- ²²R. Robbiani and J. L. Franklin, J. Am. Chem. Soc. 101,
- 764 (1979); 101, 3709 (1979).
- ²³G. E. Streit and T. W. Newton, J. Chem. Phys. 73, 3178 (1980).
- ²⁴L. M. Babcock and G. E. Streit, J. Chem. Phys. 74, 5700 (1981).
- ²⁵E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, Adv. At. Mol. Phys. 5, 1 (1969).
- ²⁶S. A. Sullivan, B. S. Freiser, and J. L. Beauchamp, Chem. Phys. Lett. 48, 294 (1977).
- ²⁷See, For example (a), D. B. Dunkin, F. C. Fehsenfeld,
- A. L. Schmeltekopf, and E. E. Ferguson, J. Chem. Phys.
- 54, 3817 (1971); (b) F. C. Fehsenfeld and E. E. Ferguson,
- J. Chem. Phys. 61, 3181 (1974).

- ²⁸D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow,
- S. M. Bailey, and R. H. Schumm, Natl. Bur. Stand. (U.S.), Tech. Note 270-3 (1967).
- ²⁹R. S. Berry and C. W. Reinmann, J. Chem. Phys. 38, 1540 (1963).
- ³⁰H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
- ³¹L. Andrews, J. Am. Chem. Soc. 98, 2147 (1976).
- ³²W. F. Howard, Jr., and L. Andrews, J. Am. Chem. Soc. 96, 7864 (1974).

J. Chem. Phys., Vol. 76, No. 5, 1 March 1982